

# Surface free energies for nematic shells

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## Abstract

We propose a continuum model to describe the molecular alignment in thin nematic shells. By contrast with previous accounts, the two-dimensional free energy, aimed at describing the physics of thin films of nematics deposited on curved substrates, is not postulated but it is deduced from the conventional three-dimensional theories of nematic liquid crystals. Both the director and the order-tensor theories are taken into account. The so-obtained surface energies exhibit extra terms compared to earlier models. These terms reflect the coupling of the geometry of the shell with the nematic order parameters. As expected, the shape of the shell plays a key role in the equilibrium configurations of nematics coating it.

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## 1 Introduction

Nematic liquid crystals are aggregates of rod-like molecules that tend to align parallel to each other along a given direction (de Gennes and Prost, 1995). Due to their easy response to externally applied electric, magnetic, optical and surface fields, liquid crystals are of greatest potential for scientific and technological applications. Currently, there is an increasing interest in soft matter physics on small spherical colloidal particles or droplets coated with a thin layer of nematic liquid crystal (Lopez-Leon et al., 2011b,a). The hope is to build *mesoatoms* with controllable valence (Nelson, 2002). We refer to these coating layers as *nematic shells*.

When nematic liquid crystals are constrained to a curved surface, the geometry induces a distortion in the molecular orientation. The possibility to have an in-plane order rather than a spatial distribution of the molecules, depends on the shell thickness (Vitelli and Nelson, 2006; Fernández-Nieves et al., 2007; Lopez-Leon et al., 2011b). In ultra-thin shells, the interaction with the colloid surface enforces a sort of degenerate anchoring, *i.e.* the tendency of the molecules to align along any direction parallel to the surface. Thus, unavoidably defects arise when nematic order is established on a surface with the topology of the sphere. The number of defects is a consequence of the Poincaré-Hopf theorem, that states that any configuration must have a total topological charge equal to the Euler-Poincaré characteristic of the surface. For instance on a sphere, whose characteristic is +2, we can have two diametrically opposite +1 defects or four +1/2 defects located at the vertices of a tetrahedron (Vitelli and Nelson,

2006). This tetrahedral defect structure is of great interest in material science because defects regions can be functionalized to serve as bonds (Nelson, 2002). This could lead to tetravalent mesoatoms with  $sp^3$ -like directional bonding like carbon. Theoretical studies have emphasized the possibility to control the location of the defects, and hence the valence of mesoatoms, by varying the shell geometry (Kralj et al., 2011) or by tuning the elastic constants of the nematic (Bates, 2008; Shin et al., 2008).

Most theoretical studies on nematic liquid crystals are framed within the classical *director theory* (see, for instance, (de Gennes and Prost, 1995; Virga, 1994)). In this setting, the local properties of the nematic liquid crystal are described through a unit vector, the director, parallel to the local molecular direction. The equilibrium configurations of the nematics minimize the Frank's free energy, with respect to all configurations that satisfy the boundary conditions. However, the director description of a nematic configuration misses a relevant information at the mesoscopic level: the dispersion of the molecules around the director. The *order-tensor theory*, put forward by de Gennes (see de Gennes and Prost (1995); Virga (1994)), overcomes this gap by introducing a richer kinematic description. Within this theory the free energy to minimize is the Landau-de Gennes free energy.

Theories for two-dimensional nematic order have been proposed in both director and order-tensor schemes (Straley, 1971; Helfrich and Prost, 1988; Lubensky and MacKintosh, 1993; Selinger et al., 2001; Biscari and Terentjev, 2006; Kralj et al., 2011) and use free energies derived by symmetry arguments or mesoscopic properties. By contrast, our approach derives the surface free energy for thin films as limiting cases of the well established three-dimensional theories of nematic liquid crystals. The main concern is how classical theories (Frank and Landau-de Gennes theories) reduce when the nematic molecules, confined within a thin region, align in the direction parallel to the underlying surface. A prominent role is played by the ratio between the thickness of the shell, denoted by  $h$ , and the minimum radius of curvature of the entire shell, denoted by  $\ell$ . In fact, the surface versions of Frank and Landau-de Gennes free energies can be deduced from the three-dimensional models under the assumption of smallness of the ratio  $h/\ell$ .

Conversely to existing models, we find that in the two-dimensional director theory the twist term does not vanish. Actually, it expresses the tendency of the molecular axis to align with the principal directions. Moreover, our analysis provides a coherent way to obtain the two-dimensional order-tensor theory. As a result, we retrieve the quadrupolar coupling between the two-dimensional order tensor and the curvature tensor already obtained by Biscari and Terentjev (2006) using mesoscopic arguments.

The paper is organized as follows. In Section 2, we introduce the mathematical notation and terminology. Sections 3 and 4, are devoted to obtain surface free energies from Frank and Landau-de Gennes theories, respectively. Mathematical topics employed in these sections and some details of the calculations are reported in the Appendixes. Finally, we draw our conclusive remarks in Section 5.

## 2 Geometrical preliminaries

We first introduce the terminology and establish some preliminary notations. First of all, three-dimensional vectors are denoted by lower-case boldface letters, whereas second order tensors are denoted by upper-case boldface letters. The scalar, vector and tensor products between two vectors  $\mathbf{u}$  and  $\mathbf{v}$  are indicated by  $\mathbf{u} \cdot \mathbf{v}$ ,  $\mathbf{u} \times \mathbf{v}$  and  $\mathbf{u} \otimes \mathbf{v}$ , respectively. In cartesian components,  $\mathbf{u} \cdot \mathbf{v} = u_i v_i$ ,  $(\mathbf{u} \times \mathbf{v})_i = \epsilon_{ijk} u_j v_k$ ,  $(\mathbf{u} \otimes \mathbf{v})_{ij} = u_i v_j$ , where summation is understood over repeated indices, and the third order tensor  $\boldsymbol{\epsilon} = \epsilon_{ijk}$  is the Ricci alternator. The composition between two second-order tensors  $\mathbf{A}$  and  $\mathbf{B}$  is the tensor  $\mathbf{C} = \mathbf{AB}$  with components  $C_{ij} = A_{ih} B_{hj}$ , whereas the composition between a second order tensor  $\mathbf{A}$  and a vector  $\mathbf{u}$  gives the vector  $\mathbf{v} = \mathbf{Au}$  with components  $v_i = A_{ij} u_j$ . Finally, the scalar product between  $\mathbf{A}$  and  $\mathbf{B}$  is the

scalar  $A_{ij}B_{ij}$ .

Let us assume that the nematic shell occupies a thin region  $V$  of thickness  $h$  around a regular compact surface  $\mathcal{S}$ . Let  $\boldsymbol{\nu}_s$  be the normal unit vector field to  $\mathcal{S}$ . We parameterize points in the bulk through a coordinate set  $(u, v, \xi)$  such that

$$p(u, v, \xi) = p_S(u, v) + \xi \boldsymbol{\nu}_s(u, v), \quad (1)$$

where  $p_S$  is the normal projection of  $p$  onto  $\mathcal{S}$ , and  $|\xi|$ , with  $\xi \in [-h/2, h/2]$ , is the distance of  $p$  from the same surface. Such a coordinate set is well defined in a finite neighborhood of  $\mathcal{S}$ . More precisely, we introduce the principal curvatures  $c_{1s}(p_S)$  and  $c_{2s}(p_S)$  of  $\mathcal{S}$  at point  $p_S$ , and assume

$$h \ll \min_{p_S \in \mathcal{S}} (\max\{|c_{1s}(p_S)|, |c_{2s}(p_S)|\})^{-1} = \ell. \quad (2)$$

For every fixed  $\xi \in [-h/2, h/2]$ , equation (1) defines a parallel surface  $\mathcal{S}_\xi = \{p_S + \xi \boldsymbol{\nu}_s(p_S) : p_S \in \mathcal{S}\}$  at distance  $|\xi|$  from  $\mathcal{S}$  with the vector field  $\boldsymbol{\nu} : p \in \mathcal{S}_\xi \mapsto \boldsymbol{\nu}_s(p_S)$  as unit normal vector field. In such a way, the unit vector field  $\boldsymbol{\nu}$  is defined on the entire region  $V$ . The second-order tensor  $\nabla \boldsymbol{\nu}$  is symmetric. Its eigenvectors are  $\boldsymbol{\nu}$  (with a null eigenvalue) and the unit vector fields

$$\mathbf{e}_i(p) = \mathbf{e}_{is}(p_S) \quad (i = 1, 2),$$

where  $\mathbf{e}_{1s}$  and  $\mathbf{e}_{2s}$  represent the tangent principal directions fields on  $\mathcal{S}$ . The spatial gradient for each eigenvector is

$$\nabla \boldsymbol{\nu} = -\frac{c_{1s}}{1 - \xi c_{1s}} \mathbf{e}_1 \otimes \mathbf{e}_1 - \frac{c_{2s}}{1 - \xi c_{2s}} \mathbf{e}_2 \otimes \mathbf{e}_2, \quad (3)$$

$$\nabla \mathbf{e}_1 = \kappa_1(\xi) \mathbf{e}_2 \otimes \mathbf{e}_1 + \kappa_2(\xi) \mathbf{e}_2 \otimes \mathbf{e}_2 + \frac{c_{1s}}{1 - \xi c_{1s}} \boldsymbol{\nu} \otimes \mathbf{e}_1, \quad (4)$$

$$\nabla \mathbf{e}_2 = -\kappa_1(\xi) \mathbf{e}_1 \otimes \mathbf{e}_1 - \kappa_2(\xi) \mathbf{e}_1 \otimes \mathbf{e}_2 + \frac{c_{2s}}{1 - \xi c_{2s}} \boldsymbol{\nu} \otimes \mathbf{e}_2, \quad (5)$$

where the functions  $\kappa_1$  and  $\kappa_2$  are given in Appendix A. We refer the reader to the book of do Carmo (1976) for a more comprehensive treatise of the geometry of surfaces.

Let  $\Phi$  be a smooth field defined on  $\mathcal{S}$ . Assume  $\Phi$  scalar, vector or tensor valued. Then the surface gradient of  $\Phi$  is defined (see Gurtin and Murdoch (1975)) as

$$\nabla_s \Phi = (\nabla \Phi) \mathbf{P},$$

where  $\mathbf{P} = \mathbf{I} - \boldsymbol{\nu}_s \otimes \boldsymbol{\nu}_s$  represents the projection onto the tangent plane of  $\mathcal{S}$ . The trace of the surface gradient of a vector field  $\mathbf{u}$  defines the surface divergence of  $\mathbf{u}$ :  $\text{div}_s \mathbf{u} = \text{tr} \nabla_s \mathbf{u} = \nabla_s \mathbf{u} \cdot \mathbf{P}$ , that is a scalar field. On the other hand, the surface curl of  $\mathbf{u}$  is defined as twice the skew-symmetric part of the surface gradient:

$$\text{curl}_s \mathbf{u} = -\epsilon \nabla_s \mathbf{u},$$

where  $\epsilon$  denotes the Ricci alternator.

Let  $\mathbf{n}$  denote a unit vector field defined on  $V$  such that  $\mathbf{n}(p) = \mathbf{n}(p_S)$  and  $\mathbf{n} \cdot \boldsymbol{\nu} = 0$  at each point  $p$ . Next, by introducing the *conormal* unit vector field  $\mathbf{t} = \boldsymbol{\nu} \times \mathbf{n}$ , we write the spatial gradient of  $\mathbf{n}$  (see Appendix A for calculation details):

$$\begin{aligned} \nabla \mathbf{n} = & \iota^{-1} \left\{ [\kappa_{\mathbf{n}_s} - \xi \boldsymbol{\nu}_s \cdot \text{curl}_s(\mathbf{L} \mathbf{n}_s)] \mathbf{t} \otimes \mathbf{n} + [\kappa_{\mathbf{t}_s} - \xi \boldsymbol{\nu}_s \cdot \text{curl}_s(\mathbf{L} \mathbf{t}_s)] \mathbf{t} \otimes \mathbf{t} \right. \\ & \left. + (c_{\mathbf{n}_s} - \xi K) \boldsymbol{\nu} \otimes \mathbf{n} - \tau_{\mathbf{n}_s} \boldsymbol{\nu} \otimes \mathbf{t} \right\}, \end{aligned} \quad (6)$$

where  $\mathbf{n}_s$  and  $\mathbf{t}_s$  represent the restrictions of  $\mathbf{n}$  and  $\mathbf{t}$  on  $\mathcal{S}$ , respectively. The tensor  $\mathbf{L} = -\nabla_s \boldsymbol{\nu}_s$  represents the extrinsic curvature tensor of  $\mathcal{S}$ . Its trace gives twice the mean curvature  $H$ , while its determinant gives the Gaussian curvature  $K$ . The quantities  $c_{\mathbf{n}_s} = \mathbf{n}_s \cdot \mathbf{L} \mathbf{n}_s$ ,  $\tau_{\mathbf{n}_s} = -\mathbf{t}_s \cdot \mathbf{L} \mathbf{n}_s$  represent the normal curvature and the geodesic torsion of the flux lines of  $\mathbf{n}_s$  on  $\mathcal{S}$ , respectively. The latter is zero whenever  $\mathbf{n}_s$  is a principal direction. The quantities  $\kappa_{\mathbf{n}_s}$  and  $\kappa_{\mathbf{t}_s}$  denote the geodesic curvature of the flux lines of  $\mathbf{n}_s$  and  $\mathbf{t}_s$  on  $\mathcal{S}$ , respectively (Rosso, 2003; Tu and Ou-Yang, 2004). The geodesic curvature  $\kappa_{\mathbf{n}_s}$  (respectively,  $\kappa_{\mathbf{t}_s}$ ) measures the deviance of the flux lines of  $\mathbf{n}_s$  (respectively,  $\mathbf{t}_s$ ) from following a geodesic on  $\mathcal{S}$ . Finally, we have set  $\iota = 1 - 2H\xi + \kappa_{\mathbf{n}_s} \xi^2$ .

The divergence and the curl of  $\mathbf{n}$  are the trace of  $\nabla \mathbf{n}$  and the axial-vector associated with twice the skew-symmetric part of  $\nabla \mathbf{n}$ , respectively. Thus, from (6) it follows that

$$\operatorname{div} \mathbf{n} = \iota^{-1} [\kappa_{\mathbf{t}_s} - \xi \boldsymbol{\nu}_s \cdot \operatorname{curl}_s (\mathbf{L} \mathbf{t}_s)], \quad (7)$$

$$\operatorname{curl} \mathbf{n} = \iota^{-1} \{ -\tau_{\mathbf{n}_s} \mathbf{n} - (c_{\mathbf{n}_s} - \xi K) \mathbf{t} + [\kappa_{\mathbf{n}_s} - \xi \boldsymbol{\nu}_s \cdot \operatorname{curl}_s (\mathbf{L} \mathbf{n}_s)] \boldsymbol{\nu} \}. \quad (8)$$

We observe that the normal curvatures, the geodesic torsion, the geodesic curvatures and the surface gradients introduced above are quantities related to the surface  $\mathcal{S}$  and, therefore, they do not depend on  $\xi$ . Instead, although  $\mathbf{n}$  has been supposed constant along normal directions within the thickness, its spatial gradient depends on  $\xi$ .

Finally, since  $\kappa_{\mathbf{n}_s} = \mathbf{t}_s \cdot (\nabla_s \mathbf{n}_s) \mathbf{n}_s$  and  $\kappa_{\mathbf{t}_s} = \mathbf{t}_s \cdot (\nabla_s \mathbf{n}_s) \mathbf{t}_s$  (see Rosso (2003)), the surface gradient of  $\mathbf{n}_s$  is given by

$$\nabla_s \mathbf{n}_s = \kappa_{\mathbf{n}_s} \boldsymbol{\nu}_s \otimes \mathbf{n}_s + \kappa_{\mathbf{t}_s} \mathbf{t}_s \otimes \mathbf{t}_s + c_{\mathbf{n}_s} \boldsymbol{\nu}_s \otimes \mathbf{n}_s - \tau_{\mathbf{n}_s} \boldsymbol{\nu}_s \otimes \mathbf{t}_s,$$

and consequently

$$\operatorname{div}_s \mathbf{n}_s = \kappa_{\mathbf{t}_s}, \quad \operatorname{curl}_s \mathbf{n}_s = -\tau_{\mathbf{n}_s} \mathbf{n}_s - c_{\mathbf{n}_s} \mathbf{t}_s + \kappa_{\mathbf{n}_s} \boldsymbol{\nu}_s. \quad (9)$$

Unlike flat surfaces, the surface curl of  $\mathbf{n}_s$  possesses nonvanishing in-plane components.

### 3 Two-dimensional director theory

The classical elastic continuum theory is based on the pioneering works of Oseen, Zocher and Frank published between the thirties and the fifties of last century. We refer the reader to the book of Virga (1994) for a detailed mathematical treatment. The average alignment of the molecules is represented by a unit vector  $\mathbf{n}$ , called the director, where  $\mathbf{n}$  is physically equivalent to  $-\mathbf{n}$ . The expression for the elastic energy density (per unit of volume) associated with the director distortion consists of four terms

$$\begin{aligned} 2w_{OZF} = & K_1 (\operatorname{div} \mathbf{n})^2 + K_2 (\mathbf{n} \cdot \operatorname{curl} \mathbf{n})^2 + K_3 |\mathbf{n} \times \operatorname{curl} \mathbf{n}|^2 \\ & + (K_2 + K_{24}) \operatorname{div} [(\nabla \mathbf{n}) \mathbf{n} - (\operatorname{div} \mathbf{n}) \mathbf{n}] \end{aligned} \quad (10)$$

where the constants  $K_1$ ,  $K_2$ ,  $K_3$ , and  $K_{24}$  are called the splay, twist, bend, and saddle-splay moduli, respectively. To ensure a stable undistorted configuration of a nematic liquid crystal in the absence of external fields or confinements, the three moduli  $K_i (i = 1, 2, 3)$  must be non-negative, whereas the elastic saddle-splay constant must obey Ericksen's inequalities [6]:

$$|K_{24}| \leq K_2, \quad K_2 + K_{24} \leq 2K_1.$$

In the absence of external actions, the equilibrium configurations are stationary points of the total energy

$$W = \int_V w_{OZF}(\mathbf{n}, \nabla \mathbf{n}) dV, \quad (11)$$

according to the boundary conditions. These may consist in fixing  $\mathbf{n}$  at the boundary (strong boundary conditions) or in allowing  $\mathbf{n}$  to rotate freely (free boundary conditions). Intermediate situations, known as *weak anchoring* boundary conditions, can be envisaged by including an anchoring energy that penalizes the deviation of the molecules at the boundary from a given direction. Furthermore, the free energy density may account for extra terms in order to describe, for instance, the interaction of the nematic with external electric or magnetic fields.

Let us introduce the small parameter  $\varepsilon = h/\ell$ . The smallness of  $\varepsilon$  on the one hand ensures that the parameterization (1) is properly defined and on the other hand, with the aid of Proposition 2 (see Appendix B), it allows us to approximate the OZF free energy as follows

$$W_{OZF} \approx W_{OZF}^S = \frac{1}{2} \int_{\mathcal{S}} [k_1(\operatorname{div}_s \mathbf{n}_s)^2 + k_2(\mathbf{n}_s \cdot \operatorname{curl}_s \mathbf{n}_s)^2 + k_3|\mathbf{n}_s \times \operatorname{curl}_s \mathbf{n}_s|^2] dA, \quad (12)$$

where  $k_i = hK_i$  ( $i = 1, 2, 3$ ). Observe that the saddle-splay term has disappeared in this approximation since  $\mathbf{n}$  has assumed to be constant throughout the thickness. In fact, from (6) it follows

$$\operatorname{div}[(\nabla \mathbf{n})\mathbf{n} - (\operatorname{div} \mathbf{n})\mathbf{n}] = \operatorname{tr}(\nabla \mathbf{n})^2 - (\operatorname{tr} \nabla \mathbf{n})^2 = 0. \quad (13)$$

Comparing equations (12) and (10) we remark that: (i)  $W_{OZF}^S$  involves a surface integral rather than a volume integral, thus we can refer to  $W_{OZF}^S$  as a *surface free energy*; (ii) the surface elastic constants  $k_i$  are obtained by multiplying  $K_i$  and the thickness  $h$ , and, hence, by virtue of Ericksen's inequalities, they must be non negative; (iii) the surface free energy involves surface differential operators instead of spatial ones.

It is worth mentioning a peculiarity of curved substrates with respect to planar nematics. Unlike the planar case, the twist term cannot be a priori neglected. Indeed, as it has been already observed,  $\operatorname{curl}_s \mathbf{n}_s$  is not orthogonal to  $\mathbf{n}_s$ . In fact, by using formulae (9), equations (12) reduces to

$$W_{OZF}^S = \frac{1}{2} \int_{\mathcal{S}} [k_1 \kappa_{\mathbf{t}_s}^2 + k_2 \tau_{\mathbf{n}_s}^2 + k_3(c_{\mathbf{n}_s}^2 + \kappa_{\mathbf{n}_s}^2)] dA, \quad (14)$$

which shows that the twist free energy density is proportional to  $\tau_{\mathbf{n}_s}^2$ . The latter vanishes if and only if the flux lines of  $\mathbf{n}_s$  lie along principal directions. Thus, the twist free energy can be disregarded whenever spherical shells are concerned (Shin et al., 2008) or whenever the director lies along meridians or parallels of an axisymmetric shell (Chen and Kamien, 2009).

In light of (14), we can give the following intuitive interpretation for the shell-nematic interaction. The arrangement of the molecules on a surface is the result of the competition between the splay and the bend free energies that try to put the flux lines of  $\mathbf{n}_s$  and  $\mathbf{t}_s$  along geodesics of  $\mathcal{S}$ , and the twist term that tries to align the flux lines of  $\mathbf{n}_s$  with the curvature lines of  $\mathcal{S}$ . Furthermore, the term proportional to the square of the normal curvature, expresses the tendency of the flux lines of  $\mathbf{n}_s$  to align with the principal direction of minimal curvature.

From equation (14) it follows that within the *one constant approximation* ( $k_1 = k_2 = k_3 = k$ ), the surface OZF free energy becomes

$$W_{OZF}^S = \frac{k}{2} \int_{\mathcal{S}} |\nabla_s \mathbf{n}_s|^2 dA. \quad (15)$$

A key feature of the free energy (15) is that it differs from the one used in earlier works (Straley, 1971; Vitelli and Nelson, 2006; Tu and Seifert, 2007). Indeed, by denoting  $\alpha$  the angle between the principal direction  $\mathbf{e}_{1s}$  and  $\mathbf{n}_s$ , equation (15) reduces to

$$W_{OZF}^S = \frac{k}{2} \int_{\mathcal{S}} (|\nabla_s \alpha - \boldsymbol{\omega}|^2 + c_{\mathbf{n}_s}^2 + \tau^2) dA,$$

where  $\omega$  represents the *spin connection field* (Nelson and Peliti, 1987; Bowick and Giomi, 2009). A glance at equation (21a) of Nelson and Peliti (1987) shows that the terms proportional to  $\tau_{\mathbf{n}_s}^2$  and  $c_{\mathbf{n}_s}^2$  were neglected. Clearly, this mismatch stems from the fact that free energy density in (15) is proportional to the square of the surface gradient of  $\mathbf{n}_s$  rather than proportional to the square of covariant derivative of  $\mathbf{n}_s$  as it is customary to assume (see for instance (Nelson and Peliti, 1987) or (Tu and Seifert, 2007)).

## 4 Two-dimensional order-tensor theory

The director theory describes only states with a single optical axis. For closed shells whose topology is different from that of a torus, the tangent vector field  $\mathbf{n}$  exhibits singular points, *i.e.* regions where the local orientational order of the nematic is undefined. As a result, the shell often incorporates so-called topological defects. These mathematical singularities can be avoided by introducing a tensorial-order parameter, that describes defects as those points in which the nematic melts into a liquid phase (isotropic states). Hereinafter we illustrate the geometrical meaning of that order parameter.

We now recall the order-tensor theory for the usual three-dimensional nematics. Let us suppose that the orientation of a single molecule is represented by a unit vector  $\mathbf{m}$ . Microscopic disorder is taken into account by introducing a probability measure  $f_p : \mathbb{S}^2 \rightarrow \mathbb{R}^+$ , such that  $f_p(\mathbf{m})$  describes the probability that a molecule placed in  $p$  is oriented along  $\mathbf{m}$ . The orientation of the molecular axis is described at each point in space by a point of the unit sphere  $\mathbb{S}^2$  (or by a unit vector). Thus, if  $\Omega$  is any subset of  $\mathbb{S}^2$ , the probability of finding in  $p$  one molecule oriented within  $\Omega$  is given by

$$P\{\Omega\} = \int_{\Omega} f_p(\mathbf{m}) d\sigma,$$

where  $\sigma$  denotes the area measure on  $\mathbb{S}^2$ . Nematics possess a molecular mirror symmetry, *i.e.*, the *head* and *tail* of a molecule can be changed without experiencing any change in the probability distribution. Thus, the probability measure is even,  $f_p(\mathbf{m}) = f_p(-\mathbf{m})$ , and the first moment of the distribution  $f_p$  is zero.

The second moment of the distribution is the variance tensor  $\mathbf{M} = \langle \mathbf{m} \otimes \mathbf{m} \rangle$ , where the brackets denote averaging with respect to  $f_p$ . By definition,  $\mathbf{M}$  is unit trace symmetric and semidefinite positive. The spectral decomposition theorem ensures that  $\mathbf{M}$  can be put in the diagonal form:

$$\mathbf{M} = \lambda_1 \mathbf{e}_1 \otimes \mathbf{e}_1 + \lambda_2 \mathbf{e}_2 \otimes \mathbf{e}_2 + \lambda_3 \mathbf{e}_3 \otimes \mathbf{e}_3,$$

and, since the eigenvalues of  $\mathbf{M}$  sum up to one, its spectrum is bounded by  $\text{sp}(\mathbf{M}) \subset [0, 1]$ .

Nematics may exhibit three different states: isotropic, uniaxial, and biaxial. It is customary to define these states by using the *order tensor*  $\mathbf{Q} = \mathbf{M} - \frac{1}{3}\mathbf{I}$ . Thus, we can have:

- (i) the eigenvalues of  $\mathbf{Q}$  are equal, which implies  $\mathbf{Q}_{iso} = \mathbf{0}$ ; in this case we label the nematic as *isotropic*.
- (ii) At least two eigenvalues are equal, the nematic is called *uniaxial*. Simple algebraic manipulation allows us to write:

$$\mathbf{Q}_{uni} = s \left( \mathbf{u} \otimes \mathbf{u} - \frac{1}{3}\mathbf{I} \right).$$

The scalar parameter  $s \in [-\frac{1}{2}, 1]$  is called the *degree of orientation*, while the unit vector  $\mathbf{u}$  is the optical axis. We retrieve the isotropic phase when  $s = 0$ , while the perfect

alignment of the molecules is obtained for  $s = 1$ . The case  $s = -\frac{1}{2}$  represents flat isotropic distributions, in the plane orthogonal to  $\mathbf{u}$ .

- (iii) When the eigenvalues of the order tensor are all different, the nematic is labeled as *biaxial*. Then we can write the general expression for the order tensor

$$\mathbf{Q}_{bia} = s \left( \mathbf{u} \otimes \mathbf{u} - \frac{1}{3} \mathbf{I} \right) + \lambda (\mathbf{e}_+ \otimes \mathbf{e}_+ - \mathbf{e}_- \otimes \mathbf{e}_-),$$

where  $\lambda$  denotes the degree of biaxiality and  $s \in [-\frac{1}{2}, 1]$  as above. The sign of  $\lambda$  is unessential, since it only involves an exchange between  $\mathbf{e}_+$  and  $\mathbf{e}_-$ . The degree of biaxiality does always satisfy  $|\lambda| \leq \frac{1}{3}(1 - s)$ . Even for biaxial nematic,  $s = -\frac{1}{2}$  represents flat (non necessarily isotropic) distributions.

The free energy comprises two terms: the elastic energy and the Landau-de Gennes potential. Following Longa et al. (1987), the most general quadratic elastic energy can be written as

$$W_{el}(\nabla \mathbf{Q}, \mathbf{Q}) = \int_V [L_1 Q_{ij,k} Q_{ij,k} + L_2 Q_{ij,k} Q_{ik,j} + L_{24} (Q_{ij,k} Q_{jk} - Q_{ij} Q_{jk,k})_{,i}] dV, \quad (16)$$

where  $L_1$ ,  $L_2$  and  $L_{24}$  are constants. Here a comma denotes a partial derivative with respect to one of the coordinates. This energy expresses the tendency of the molecules to arrange parallel one to each other in a homogeneous state.

The Landau-de Gennes potential,  $W_{LdG}$ , is a temperature-dependent thermodynamic contribution that takes into account the material tendency to spontaneously arrange in ordered or disordered states. Its density is of the form (see de Gennes and Prost (1995))

$$w_{LdG}(\mathbf{Q}) = F(A, B, C) + \frac{A}{2} \text{tr} \mathbf{Q}^2 - \frac{B}{3} \text{tr} \mathbf{Q}^3 + \frac{C}{4} (\text{tr} \mathbf{Q}^2)^2, \quad (17)$$

where  $A = A_0(T - T_c)/T_c$ ,  $A_0$  is a material-dependent positive constant,  $T$  is the absolute temperature and  $T_c$  is a characteristic temperature;  $B$ ,  $C$  are material-dependent positive constants and  $F(A, B, C)$  is a positive constant that accounts for the free energy of the isotropic phase. We observe that  $F(A, B, C)$  plays no role in the minimization of the Landau-de Gennes energy density and the stationary points of  $w_{LdG}$  correspond to either isotropic tensors or, whenever  $B^2 - 24AC \geq 0$ , uniaxial tensors of the form

$$\mathbf{Q}_{cr} = \tilde{s} \left( \mathbf{u} \otimes \mathbf{u} - \frac{1}{3} \mathbf{I} \right),$$

with

$$\tilde{s} = \frac{B + \sqrt{B^2 - 24AC}}{4C},$$

and  $\mathbf{u} \in \mathbb{S}^2$ . In addition to the supercooling temperature  $T_c$  below which the isotropic state loses its stability, there are two other characteristic temperatures for  $w_{LdG}$ : the nematic-isotropic transition temperature  $\left(1 + \frac{B^2}{27A_0C}\right) T_c$  at which the nematic and the isotropic phase have the same energy, and the superheating temperature  $\left(1 + \frac{B^2}{24A_0C}\right) T_c$  above which the isotropic phase is the unique stationary point of  $w_{LdG}$ . The resulting seven characteristic temperature regimes for  $w_{LdG}$  are discussed in detail by Turzi (2007).



## 4.1 Degenerate states

The procedure to derive the two-dimensional free energy for nematic shells is performed in two subsequent steps: (a) we have to specialize the free energy to describe degenerate planar distributions, where the eigenvector of  $\mathbf{M}$  with null eigenvalue coincides with  $\boldsymbol{\nu}$ ; then, (b) as for the OZF free energy, we approximate the three-dimensional free energy under the assumption of smallness of the parameter  $\varepsilon$ .

To describe a degenerate anchoring throughout the shell, let us suppose the nematic molecules are orthogonal to  $\boldsymbol{\nu}$  and  $\mathbf{m}(p(u, v, \xi)) = \mathbf{m}(p_S(u, v))$ . Since at each point the probability to find  $\mathbf{m}$  in the direction  $\boldsymbol{\nu}$  is zero, it follows that  $\mathbf{M}\boldsymbol{\nu} = \mathbf{0}$ . This means that no isotropic spatial states are allowed. Let us introduce  $\mathbf{n}$  and  $\mathbf{t}$  the eigenvectors of  $\mathbf{M}$  orthogonal to  $\boldsymbol{\nu}$ . We write the variance tensor in the form (Kralj et al., 2011)

$$\overline{\mathbf{M}} = \frac{1}{2}(\mathbf{I} - \boldsymbol{\nu} \otimes \boldsymbol{\nu}) + \lambda(\mathbf{n} \otimes \mathbf{n} - \mathbf{t} \otimes \mathbf{t}),$$

where  $\lambda \in [-\frac{1}{2}, \frac{1}{2}]$ . We recognize that two kinds of uniaxial states are allowed: (a)  $\lambda = 0$  then  $\boldsymbol{\nu}$  is the optical axis and the molecules are randomly distributed orthogonally to  $\boldsymbol{\nu}$ ; (b)  $\lambda = \pm\frac{1}{2}$  and the molecules are perfectly ordered along a direction orthogonal to  $\boldsymbol{\nu}$ . The latter case coincides with the director theory analyzed in the previous section. Note that the sign of  $\lambda$  is inessential since, the order tensors associated with negative values of  $\lambda$  and director  $\mathbf{n}$  coincide with the order tensors associated with the positive degree of order  $-\lambda$  and director  $\mathbf{t}$ .

An alternative and equivalent parameterization of the variance tensor is the following (Biscari and Terentjev, 2006):

$$\overline{\mathbf{M}} = q(\mathbf{n} \otimes \mathbf{n}) + \frac{1}{2}(1 - q)(\mathbf{I} - \boldsymbol{\nu} \otimes \boldsymbol{\nu}), \quad (18)$$

with  $q = 2\lambda \in [-1, 1]$ .

It is worth noting that this parameterization can be also obtained from the three-dimensional order parameter  $\mathbf{M}$  by imposing  $s = -\frac{1}{2}$ , by taking  $\mathbf{u}$  along the normal surface and by choosing  $\mathbf{n}$  along one of the two tangential eigenvectors of  $\mathbf{M}$ .

## 4.2 Elastic energy

Now, let us introduce the traceless tensor  $\overline{\mathbf{Q}}$ , associated with  $\overline{\mathbf{M}}$ , in the usual way:  $\overline{\mathbf{Q}} = \overline{\mathbf{M}} - \frac{1}{3}\mathbf{I}$ . This tensor differs from the one of equation (6) in Kralj et al. (2011), which is indeed the traceless tensor obtained by subtracting from  $\overline{\mathbf{M}}$  one-half of the projector on  $\mathcal{S}$  (which is the identity on the tangent plane).

With the aim of adapting the elastic free energy to the case of degenerate states, we replace  $\mathbf{Q}$  by  $\overline{\mathbf{Q}}$ . Since  $\overline{\mathbf{Q}}$  and  $\overline{\mathbf{M}}$  (as well as  $\mathbf{Q}$  and  $\mathbf{M}$ ) differ up to a constant, we have  $\nabla \overline{\mathbf{Q}} = \nabla \overline{\mathbf{M}}$ ; thus, in the elastic energy,  $\overline{\mathbf{Q}}$  can be replaced by  $\overline{\mathbf{M}}$ .

Furthermore, by using the parameterization (18) and with the aid of equations (3-5), the following identities hold:

$$\begin{aligned} \overline{M}_{ij,k} \overline{M}_{ij,k} &= 2q^2 \{ (\operatorname{div} \mathbf{n})^2 + |\mathbf{n} \times \operatorname{curl} \mathbf{n}|^2 + (\operatorname{curl} \mathbf{n} \cdot \mathbf{n})^2 \} + \frac{1}{2} |\nabla q|^2 \\ &\quad + 2\iota^{-2} (1 - q) (H - \kappa_{\mathbf{n}_s} \xi) [(1 - q)H + 2qc_{\mathbf{n}_s} - (1 + q)\kappa_{\mathbf{n}_s} \xi] \\ &\quad - \iota^{-2} (1 - q^2) K, \end{aligned} \quad (19)$$

$$\overline{M}_{ij,k} \overline{M}_{ik,j} = (\overline{M}_{ij,k} \overline{M}_{jk} - \overline{M}_{ij} \overline{M}_{jk,k})_{,i} + \overline{M}_{ij,j} \overline{M}_{ik,k}, \quad (20)$$



$$(\overline{M}_{ij,k}\overline{M}_{jk} - \overline{M}_{ij}\overline{M}_{jk,k})_{,i} = 2q\nabla q \cdot [(\nabla \mathbf{n})\mathbf{n} - (\text{div} \mathbf{n})\mathbf{n}] + \text{div} \left\{ \frac{1-q}{2\iota} [(1-q)H + 2qc_{\mathbf{n}_s} - (1+q)\kappa_{\mathbf{n}_s} \, xi] \boldsymbol{\nu} \right\}, \quad (21)$$

$$\begin{aligned} \overline{M}_{ij,j}\overline{M}_{ik,k} &= q^2 [(\text{div} \mathbf{n})^2 + |\mathbf{n} \times \text{curl} \mathbf{n}|^2] + \frac{1}{4} |\nabla q|^2 - q\nabla q \cdot [(\nabla \mathbf{n})\mathbf{n} - (\text{div} \mathbf{n})\mathbf{n}] \\ &\quad + \iota^{-2}(1-q)(H - \kappa_{\mathbf{n}_s}\xi)[(1-q)H + 2qc_{\mathbf{n}_s} - (1+q)\kappa_{\mathbf{n}_s} \, xi]. \end{aligned} \quad (22)$$

As for the director theory, in order to obtain the elastic surface free energy, we expand the volume free energy as a power series in the small parameter  $\varepsilon$  and consider only the leading order term. Thus, by means of Proposition 1 in Appendix B, we obtain

$$\begin{aligned} W_{el}^S &= \int_S l_1 \left[ q^2 (\kappa_{\mathbf{t}_s}^2 + \kappa_{\mathbf{n}_s}^2) + \frac{1}{4} |\nabla_s q|^2 + \left( H + q \frac{c_{\mathbf{n}_s} - c_{\mathbf{t}_s}}{2} \right)^2 \right] dA \\ &\quad + \int_S l_2 q \nabla_s q \cdot (\kappa_{\mathbf{n}_s} \mathbf{t}_s - \kappa_{\mathbf{t}_s} \mathbf{n}_s) dA - \int_S l_3 (1 - q^2) \kappa_{\mathbf{n}_s} dA \\ &\quad - \int_S (l_1 + l_2 - 4l_3) q^2 \tau_{\mathbf{n}_s}^2 dA, \end{aligned} \quad (23)$$

where  $l_1 = h(2L_1 + L_2)$ ,  $l_2 = h(L_2 + 2L_{24})$ ,  $l_3 = h(2L_1 + L_2 + L_{24})/2$ . In the next section we show that these elastic constants are subject to restrictions in order to guarantee the positiveness of the elastic free energy.

In order to interpret the contributions of the different terms, we first examine the special case where the perfect uniaxial nematic order ( $q = 1$  everywhere) is enforced on the entire shell. Equation (23) reduces to

$$W_{el}^S(q = 1) = \int_S [l_1 (\kappa_{\mathbf{t}_s}^2 + \kappa_{\mathbf{n}_s}^2 + c_{\mathbf{n}_s}^2) - (l_1 + l_2 - 4l_3) \tau_{\mathbf{n}_s}^2] dA,$$

that represents a Frank-like surface free energy (to be compared with equation (14)). The ratio between the twist and the splay constants can be tuned acting on the constant  $l_i$ . In particular, when  $L_2 = 0$ , then  $4l_3 = 2l_1 + l_2$ , and we retrieve the one constant approximation of the Frank's energy (15).

By denoting  $\mathbf{M}_s = q(\mathbf{n}_s \otimes \mathbf{n}_s) + \frac{1}{2}(1-q)\mathbf{P}$  the restriction of  $\overline{\mathbf{M}}$  to  $\mathcal{S}$ , the following identity holds

$$l_1 \left( H + q \frac{c_{\mathbf{n}_s} - c_{\mathbf{t}_s}}{2} \right)^2 = l_1 (\mathbf{M}_s \cdot \mathbf{L})^2; \quad (24)$$

the right hand side of this identity is the quadrupolar coupling between the curvature tensor and the surface order tensor derived in Biscari and Terentjev (2006) employing quasi-microscopic arguments. When  $q$  is different from zero, this term express the tendency of  $\mathbf{n}_s$  to align along one of the two principal directions depending on the sign of the mean curvature.

The energy term proportional to the square of surface gradient of  $q$  clearly expresses the tendency of the nematic to arrange in states with constant order parameter. It is worth to note that, for topological reasons, states with non zero uniform  $q$  are not always allowed. This is the case of closed surfaces with the topology of the sphere.

The term proportional to Gaussian curvature  $K$  was already obtained in Kralj et al. (2011). It is a constant term only when  $q$  is homogeneous on a fixed surface, by virtue of Gauss-Bonnet theorem.

Concerning the second integral of the right hand side of (23), we find the following identity (see Appendix C)

$$\int_S q(\nabla_s q) \cdot (\kappa_{\mathbf{n}_s} \mathbf{t}_s - \kappa_{\mathbf{t}_s} \mathbf{n}_s) dA = \frac{1}{2} \int_{\partial S} q^2 (\nabla_s \alpha - \boldsymbol{\omega}) \cdot d\mathbf{l} + \frac{1}{2} \int_S q^2 K dA, \quad (25)$$

with  $\alpha$  and  $\boldsymbol{\omega}$  as in previous section. Thus, for closed shells, the density free energy density associated with this term is even proportional to the Gaussian curvature.

#### 4.2.1 Restrictions on the elastic coefficients

The positiveness of the free energy imposes suitable restrictions to the free energy coefficients. Following the approach pursued in Kralj et al. (2011), let us decompose the surface elastic free energy density  $w_{el}^S$  as follows

$$w_{el}^S = w_{el1}^S + w_{el2}^S + w_{el3}^S, \quad (26)$$

with

$$w_{el1}^S = l_1 \left[ q^2 (\kappa_{\mathbf{t}_s}^2 + \kappa_{\mathbf{n}_s}^2) + \frac{1}{4} |\nabla_s q|^2 \right] + l_2 q (\kappa_{\mathbf{n}_s} \mathbf{t}_s - \kappa_{\mathbf{t}_s} \mathbf{n}_s) \cdot \nabla_s q, \quad (27)$$

$$w_{el2}^S = \frac{l_1}{4} [(1+q)^2 c_{\mathbf{n}_s}^2 + 2(1-q^2) c_{\mathbf{n}_s} c_{\mathbf{t}_s} + (1-q)^2 c_{\mathbf{t}_s}^2] - l_3 (1-q^2) c_{\mathbf{n}_s} c_{\mathbf{t}_s}, \quad (28)$$

$$w_{el3}^S = [l_3 - (l_1 + l_2 - 3l_3) q^2] \tau_{\mathbf{n}_s}^2, \quad (29)$$

where the identity  $\kappa_{\mathbf{n}_s} = c_{\mathbf{n}_s} c_{\mathbf{t}_s} - \tau_{\mathbf{n}_s}^2$  has been used. Then, we recognize that  $w_{el1}^S = \mathbf{v}_1 \cdot \mathbf{A}_1 \mathbf{v}_1$  and  $w_{el2}^S = \mathbf{v}_2 \cdot \mathbf{A}_2 \mathbf{v}_2$ , with

$$\mathbf{A}_1 = \begin{pmatrix} l_1 & l_2/2 & 0 & 0 \\ l_2/2 & l_1/4 & 0 & 0 \\ 0 & 0 & l_1 & -l_2/2 \\ 0 & 0 & -l_2/2 & l_1/4 \end{pmatrix}, \quad \mathbf{A}_2 = \frac{1}{4} \begin{pmatrix} l_1 & l_1 - 2l_3 \\ l_1 - 2l_3 & l_1 \end{pmatrix},$$

$$\mathbf{v}_1 := (q\kappa_{\mathbf{n}_s}, \nabla_s q \cdot \mathbf{t}_s, q\kappa_{\mathbf{t}_s}, \nabla_s q \cdot \mathbf{n}_s), \quad \mathbf{v}_2 := [(1+q)c_{\mathbf{n}_s}, (1-q)c_{\mathbf{t}_s}].$$

Hence, it can be easily proved that  $w_{el}^S \geq 0$  if and only if

$$l_1 \geq 0, \quad |l_2| \leq l_1, \quad 0 \leq l_3 \leq l_1, \quad l_1 + l_2 \leq 4l_3,$$

or, equivalently,

$$L_1 \geq 0, \quad 2L_1 + L_2 \geq 0, \quad |L_{24}| \leq 2L_1 + L_2, \quad |L_2 + 2L_{24}| \leq 2L_1 + L_2. \quad (30)$$

By assuming  $L_1 > 0$  and introducing the ratios  $\lambda_1 = L_2/L_1$  and  $\lambda_2 = L_{24}/L_1$ , the admissible region in the  $(\lambda_1, \lambda_2)$ -plane in which the surface elastic energy density (23) is positive semidefinite, is sketched in figure 1. It is worth noting that the domain in which the elastic free energy density (26) is positive semidefinite contains the domain of nonnegativeness of the surface energy density introduced in Kralj et al. (2011). This in turn contains the domain of nonnegativeness of the elastic energy density (16).

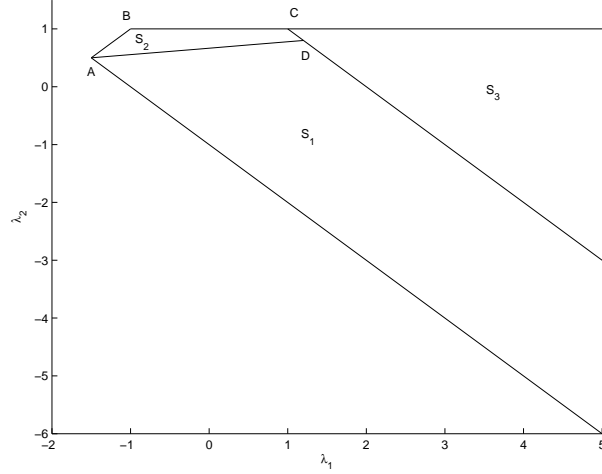


Figure 1: We have set  $\lambda_1 = L_2/L_1$ ,  $\lambda_2 = L_{24}/L_1$ .  $S_1$  is the region in which the elastic energy density in (16) is nonnegative (see Longa et al. (1987));  $S_1 \cup S_2$  represent the domain in which the surface elastic free energy in Kralj et al. (2011) is nonnegative; finally  $S_1 \cup S_2 \cup S_3$  is the region where inequalities the (30) hold.  $A \equiv (-3/2, 1/2)$ ,  $B \equiv (-1, 1)$ ,  $C \equiv (1, 1)$ ,  $D \equiv (6/5, 4/5)$ .

### 4.3 Landau-de Gennes potential

Let us consider the Landau-de Gennes free energy density (17), where  $\mathbf{Q} = \overline{\mathbf{Q}}$ . A straightforward calculation gives

$$\text{tr}(\overline{\mathbf{Q}}^2) = \frac{1}{6} + \frac{1}{2}q^2, \quad \text{tr}(\overline{\mathbf{Q}}^3) = -\frac{1}{36} + \frac{1}{4}q^2.$$

Following the same arguments given in Appendix B, we readily derive the surface Landau-de Gennes free energy

$$W_{LdG} \approx W_{LdG}^S = \int_S \left( d + \frac{a}{4}q^2 + \frac{c}{8}q^4 \right) dA \quad \text{for } \varepsilon \ll 1,$$

where

$$d = h \left[ F(A, B, C) + \frac{A}{12} + \frac{B}{108} + \frac{C}{144} \right], \quad a = a_0 \frac{T - T_c^*}{T_c}, \quad a_0 = hA_0,$$

$$c = h \frac{C}{2}, \quad T_c^* = \left( 1 + \frac{B}{3A_0} - \frac{C}{6A_0} \right) T_c.$$

We then obtain a Landau-de Gennes potential with two constants in which the cubic term vanishes. An analogous expression is proposed in Biscari and Terentjev (2006); Kralj et al. (2011). It is worth noting that, homogenous states with  $q \neq 0$  are allowed only on surfaces with zero Euler-Poincaré characteristic. In fact, only in this case it is possible to define a critical temperature that generally depends on the shell curvature.

## 5 Concluding remarks

We have deduced the two-dimensional versions of Frank and Landau-de Gennes free energies needed to treat the equilibrium of thin nematic films, coating curved surfaces. These models have been obtained as limiting cases of the respective three-dimensional models. The formalism

proposed applies to rigid shells as well as to flexible surfaces with two-dimensional nematic order. Obviously, in the latter case additional energy terms are required to describe the elasticity of the shell. The problem of equilibrium can be framed in the general variational scheme proposed in Napoli and Vergori (2010). However, the resulting equations for this complex problem are strongly non linear and demand a numerical treatment.

Our rigorous procedure predicts the existence of new terms in the free energy, with respect to earlier models. The physical interpretation of these extra terms is widely discussed in Sect. 3 and Sect. 4. The key results of our analysis are as follows:

- (i) In the context of the director theory for curved nematic thin films, the twist free energy does not vanish. This free energy, coupled with the term proportional to  $c_{\mathbf{n}_s}^2$ , expresses the tendency of the molecules to align along the principal direction of the surface with minimum curvature. Thus, the extrinsic geometry of the shell influences the molecular alignment in agreement with the results announced in Mbanga et al. (2011). In a forthcoming work, we show how the twist term influences the stability of a nematic on a toroidal surface.
- (ii) In the context of Landau-de Gennes theory, we establish a coherent framework to develop a two-dimensional order-tensor theory. As a result, we obtain the coupling term (24). This term has been already proposed in Biscari and Terentjev (2006), but it required an additional phenomenological constant in the model. By contrast, since we deduce that the coefficient of this energy is the Frank's constant  $k_1$ , no further phenomenological constants should be introduced. We notice that, within the model proposed Kralj et al. (2011), this term does not appear; this implies the counterintuitive fact that the biaxiality axes can be interchanged without affecting the energy.

Our approach offers the two-fold advantage of being based on well-established theories and, at same time, to avoid the proliferation of phenomenological coefficients in the free energy expression. Therefore, our models describe in an *economical* and *exhaustive* manner the equilibrium configuration of in-plane curved nematics. Obviously, our procedure can be extended to more complicated models as that proposed in Longa et al. (1987).

We believe that the results outlined in this paper are the basis to study the arrangement of two-dimensional curved nematics. We envisage a series of future studies to establish the influence of external actions (temperature, electric or magnetic fields), of the shell geometry, and of the material coefficients on the nematic shell texture.

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## A Derivation of the spatial gradients of $\boldsymbol{\nu}$ , $\mathbf{e}_1$ , $\mathbf{e}_2$ and $\mathbf{n}$

Let  $\boldsymbol{\varphi} = \boldsymbol{\varphi}(u, v)$  an orthogonal parameterization of  $\mathcal{S}$  such that

$$\frac{\boldsymbol{\varphi}_{,u}}{|\boldsymbol{\varphi}_{,u}|} = \mathbf{e}_{1s} \quad \text{and} \quad \frac{\boldsymbol{\varphi}_{,v}}{|\boldsymbol{\varphi}_{,v}|} = \mathbf{e}_{2s}.$$

Then, for any fixed  $\xi \in [-h/2, h/2]$ ,  $\boldsymbol{\varphi}_\xi = \boldsymbol{\varphi}(u, v) + \xi \boldsymbol{\nu}_s(u, v)$  is an orthogonal parameterization of  $\mathcal{S}_\xi$  such that

$$\boldsymbol{\varphi}_{\xi,u} = (1 - \xi c_{1s}) \boldsymbol{\varphi}_{,u} \quad \text{and} \quad \boldsymbol{\varphi}_{\xi,v} = (1 - \xi c_{2s}) \boldsymbol{\varphi}_{,v}.$$

As consequences of assumption (2) ,  $\{\mathbf{e}_1, \mathbf{e}_2\}$ , with

$$\mathbf{e}_1(p) := \frac{\boldsymbol{\varphi}_{\xi,u}}{|\boldsymbol{\varphi}_{\xi,u}|} = \frac{\boldsymbol{\varphi}_{,u}}{|\boldsymbol{\varphi}_{,u}|} = \mathbf{e}_{1s}(p_S) \quad \forall p \in V \quad (31)$$

and

$$\mathbf{e}_2(p) := \frac{\boldsymbol{\varphi}_{\xi,v}}{|\boldsymbol{\varphi}_{\xi,v}|} = \frac{\boldsymbol{\varphi}_{,v}}{|\boldsymbol{\varphi}_{,v}|} = \mathbf{e}_{2s}(p_S) \quad \forall p \in V, \quad (32)$$

is a local orthonormal basis of the space of tangent vectors  $\mathfrak{X}(\mathcal{S}_\xi)$ , whereas

$$\boldsymbol{\nu}(p) := \frac{\boldsymbol{\varphi}_{\xi,u} \times \boldsymbol{\varphi}_{\xi,v}}{|\boldsymbol{\varphi}_{\xi,u} \times \boldsymbol{\varphi}_{\xi,v}|} = \frac{\boldsymbol{\varphi}_{,u} \times \boldsymbol{\varphi}_{,v}}{|\boldsymbol{\varphi}_{,u} \times \boldsymbol{\varphi}_{,v}|} = \boldsymbol{\nu}_s(p_S) \quad \forall p \in V \quad (33)$$

is the unit normal vector field on  $\mathcal{S}_\xi$ . We now introduce the following quantities

$$\begin{aligned} e_\xi &= -\boldsymbol{\nu}_{s,u} \cdot \boldsymbol{\varphi}_{\xi,u} = c_{1s}(1 - \xi c_{1s})\boldsymbol{\varphi}_{,u} \cdot \boldsymbol{\varphi}_{,u} = c_{1s}(1 - \xi c_{1s})E, \\ f_\xi &= -\boldsymbol{\nu}_{s,u} \cdot \boldsymbol{\varphi}_{\xi,v} = 0 = -\boldsymbol{\nu}_{s,v} \cdot \boldsymbol{\varphi}_{\xi,u}, \\ g_\xi &= -\boldsymbol{\nu}_{s,v} \cdot \boldsymbol{\varphi}_{\xi,v} = c_{2s}(1 - \xi c_{2s})\boldsymbol{\varphi}_{,v} \cdot \boldsymbol{\varphi}_{,v} = c_{2s}(1 - \xi c_{2s})G, \\ E_\xi &= \boldsymbol{\varphi}_{\xi,u} \cdot \boldsymbol{\varphi}_{\xi,u} = (1 - \xi c_{1s})^2 \boldsymbol{\varphi}_{,u} \cdot \boldsymbol{\varphi}_{,u} = (1 - \xi c_{1s})^2 E, \\ F_\xi &= \boldsymbol{\varphi}_{\xi,u} \cdot \boldsymbol{\varphi}_{\xi,v} = (1 - \xi c_{1s})(1 - \xi c_{2s})\boldsymbol{\varphi}_{,u} \cdot \boldsymbol{\varphi}_{,v} = 0, \\ G_\xi &= \boldsymbol{\varphi}_{\xi,v} \cdot \boldsymbol{\varphi}_{\xi,v} = (1 - \xi c_{2s})^2 \boldsymbol{\varphi}_{,v} \cdot \boldsymbol{\varphi}_{,v} = (1 - \xi c_{2s})^2 G, \end{aligned}$$

where  $E = \boldsymbol{\varphi}_{,u} \cdot \boldsymbol{\varphi}_{,u}$  and  $G = \boldsymbol{\varphi}_{,v} \cdot \boldsymbol{\varphi}_{,v}$ .

We first derive the gradient of  $\boldsymbol{\nu}$ . From (33) it follows that

$$(\nabla \boldsymbol{\nu})\boldsymbol{\nu} = \mathbf{0}, \quad (34)$$

and, since it is a unit vector field,

$$\boldsymbol{\nu} \cdot (\nabla \boldsymbol{\nu})\mathbf{e}_i = 0 \quad \forall i = 1, 2.$$

Moreover, for any fixed  $\xi$ ,  $-\nabla \boldsymbol{\nu}$  restricted to the space of tangent vectors  $\mathfrak{X}(\mathcal{S}_\xi)$  represents the extrinsic curvature tensor of  $\mathcal{S}_\xi$ . Therefore, following do Carmo (1976):

$$\begin{aligned} \mathbf{e}_1 \cdot (\nabla \boldsymbol{\nu})\mathbf{e}_1 &= -\frac{f_\xi F_\xi - e_\xi G_\xi}{E_\xi G_\xi - F_\xi^2} = -\frac{c_{1s}}{1 - \xi c_{1s}}, \\ \mathbf{e}_1 \cdot (\nabla \boldsymbol{\nu})\mathbf{e}_2 &= -\frac{g_\xi F_\xi - f_\xi G_\xi}{E_\xi G_\xi - F_\xi^2} = 0, \\ \mathbf{e}_2 \cdot (\nabla \boldsymbol{\nu})\mathbf{e}_1 &= -\frac{e_\xi F_\xi - f_\xi E_\xi}{E_\xi G_\xi - F_\xi^2} = 0, \\ \mathbf{e}_2 \cdot (\nabla \boldsymbol{\nu})\mathbf{e}_2 &= -\frac{f_\xi F_\xi - g_\xi E_\xi}{E_\xi G_\xi - F_\xi^2} = -\frac{c_{2s}}{1 - \xi c_{2s}}, \end{aligned} \quad (35)$$

by which we deduce that  $\mathbf{e}_1$  and  $\mathbf{e}_2$  are the tangent principal directions on  $\mathcal{S}_\xi$ . Finally, (34)-(35) yield (3).

Let us now calculate  $\nabla \mathbf{e}_i$  ( $i = 1, 2$ ). From (31), (32) and since  $\mathbf{e}_i$  ( $i = 1, 2$ ) are unit vector fields, we deduce that

$$(\nabla \mathbf{e}_i)\boldsymbol{\nu} = \mathbf{0} = (\nabla \mathbf{e}_i)^T \mathbf{e}_i \quad \forall i = 1, 2. \quad (36)$$

Next, since  $\{\mathbf{e}_1, \mathbf{e}_2, \boldsymbol{\nu}\}$  is a local orthonormal basis

$$(\nabla \mathbf{e}_i)^T \mathbf{e}_j = -(\nabla \mathbf{e}_j)^T \mathbf{e}_i \quad \forall i, j = 1, 2, \quad i \neq j, \quad (37)$$

and

$$\boldsymbol{\nu} \cdot (\nabla \mathbf{e}_i) \mathbf{e}_j = -\mathbf{e}_j \cdot (\nabla \boldsymbol{\nu})^T \mathbf{e}_i = \delta_{ij} \frac{c_i}{1 - \xi c_i} \quad \forall i, j = 1, 2, \quad (38)$$

where  $\delta_{ij}$  denotes the Kronecker symbol. By means of (37),

$$\begin{aligned} \mathbf{e}_2 \cdot (\nabla \mathbf{e}_1) \mathbf{e}_1 &= -\mathbf{e}_1 \cdot (\nabla \mathbf{e}_2) \mathbf{e}_1 = \kappa_1(\xi), \\ \mathbf{e}_2 \cdot (\nabla \mathbf{e}_1) \mathbf{e}_2 &= -\mathbf{e}_1 \cdot (\nabla \mathbf{e}_2) \mathbf{e}_2 = \kappa_2(\xi), \end{aligned} \quad (39)$$

where  $\kappa_1(\xi)$  and  $\kappa_2(\xi)$  are the geodesic curvatures of the lines of curvature on  $\mathcal{S}_\xi$ . Hence, by following do Carmo (1976) and since the surface gradient of a scalar-valued function  $f$  defined in a neighborhood of  $\mathcal{S}$  may be written as

$$\nabla_s f = \frac{f_{,u}}{\sqrt{E}} \mathbf{e}_{1s} + \frac{f_{,v}}{\sqrt{G}} \mathbf{e}_{2s}, \quad (40)$$

the geodesic curvatures of the lines of curvature on  $\mathcal{S}_\xi$  are found to be

$$\begin{aligned} \kappa_1(\xi) &= -\frac{E_{\xi,v}}{2E_\xi \sqrt{G_\xi}} = -\frac{E_{,v}}{2(1 - \xi c_{2s})E\sqrt{G}} + \frac{\xi c_{1,v}}{(1 - \xi c_{1s})(1 - \xi c_{2s})\sqrt{G}} \\ &= \frac{\kappa_{1s}}{1 - \xi c_{2s}} + \frac{\xi \nabla_s c_{1s} \cdot \mathbf{e}_{2s}}{(1 - \xi c_{1s})(1 - \xi c_{2s})}, \end{aligned} \quad (41)$$

and

$$\begin{aligned} \kappa_2(\xi) &= \frac{G_{\xi,u}}{2G_\xi \sqrt{E_\xi}} = \frac{G_{,u}}{2(1 - \xi c_{1s})G\sqrt{E}} - \frac{\xi c_{2,u}}{(1 - \xi c_{1s})(1 - \xi c_{2s})\sqrt{E}} \\ &= \frac{\kappa_{2s}}{1 - \xi c_{1s}} - \frac{\xi \nabla_s c_{2s} \cdot \mathbf{e}_{1s}}{(1 - \xi c_{1s})(1 - \xi c_{2s})}, \end{aligned} \quad (42)$$

where

$$\kappa_{1s} = -\frac{E_{,v}}{2E\sqrt{G}} \quad \text{and} \quad \kappa_{2s} = \frac{G_{,u}}{2G\sqrt{E}}$$

are the geodesic curvatures of the lines of curvature on  $\mathcal{S}$ . Therefore, (36)–(42) give (4) and (5).

We are now in position to derive the gradient of the director field  $\mathbf{n}$ . Since  $\mathbf{n}$  is a unit vector field that does not vary with  $\xi$  and is pointwise orthogonal to  $\boldsymbol{\nu}$ , we get

$$(\nabla \mathbf{n}) \boldsymbol{\nu} = \mathbf{0} = (\nabla \mathbf{n})^T \mathbf{n}. \quad (43)$$

Next, we introduce the angle  $\alpha$  that  $\mathbf{n}$  form with  $\mathbf{e}_1$  so that we may write

$$\mathbf{n} = \cos \alpha \mathbf{e}_1 + \sin \alpha \mathbf{e}_2, \quad \mathbf{t} = \boldsymbol{\nu} \times \mathbf{n} = -\sin \alpha \mathbf{e}_1 + \cos \alpha \mathbf{e}_2 \quad (44)$$

and

$$\nabla \mathbf{n} = -\sin \alpha \mathbf{e}_1 \otimes \nabla \alpha + \cos \alpha \nabla \mathbf{e}_1 + \cos \alpha \mathbf{e}_2 \otimes \nabla \alpha + \sin \alpha \nabla \mathbf{e}_2. \quad (45)$$

Since  $\mathbf{n}$  and  $\mathbf{e}_1$  are constant throughout the thickness, also the scalar field  $\alpha$  satisfies the equality  $\alpha(p) = \alpha(p_S)$  for all  $p \in V$ . Therefore, in view of (40) the spatial gradient of the scalar field  $\alpha$  is

$$\begin{aligned} \nabla \alpha &= \frac{\alpha_{,u}}{(1 - \xi c_{1s})\sqrt{E}} \mathbf{e}_1 + \frac{\alpha_{,v}}{(1 - \xi c_{2s})\sqrt{G}} \mathbf{e}_2 \\ &= \frac{\nabla_s \alpha \cdot \mathbf{e}_{1s}}{1 - \xi c_{1s}} \mathbf{e}_1 + \frac{\nabla_s \alpha \cdot \mathbf{e}_{2s}}{1 - \xi c_{2s}} \mathbf{e}_2 \end{aligned}$$

Thus,

$$\begin{aligned}\boldsymbol{\nu} \cdot (\nabla \mathbf{n}) \mathbf{n} &= -\mathbf{n} \cdot (\nabla \boldsymbol{\nu}) \mathbf{n} = \frac{c_{1s} \cos^2 \alpha + c_{2s} \sin^2 \alpha - \xi c_{1s} c_{2s}}{(1 - \xi c_{1s})(1 - \xi c_{2s})} \\ &= \frac{c_{\mathbf{n}_s} - \xi K}{1 - 2\xi H + \xi^2 K},\end{aligned}\quad (46)$$

$$\boldsymbol{\nu} \cdot (\nabla \mathbf{n}) \mathbf{t} = -\mathbf{n} \cdot (\nabla \boldsymbol{\nu}) \mathbf{t} = \frac{(c_{2s} - c_{1s}) \sin \alpha \cos \alpha}{(1 - \xi c_{1s})(1 - \xi c_{2s})} = -\frac{\tau_{\mathbf{n}_s}}{1 - 2\xi H + \xi^2 K}, \quad (47)$$

$$\begin{aligned}\mathbf{t} \cdot (\nabla \mathbf{n}) \mathbf{n} &= \frac{(\nabla_s \alpha \cdot \mathbf{e}_{1s}) \cos \alpha + (\nabla_s \alpha \cdot \mathbf{e}_{2s}) \sin \alpha + \kappa_{1s} \cos \alpha + \kappa_{2s} \sin \alpha}{(1 - \xi c_{1s})(1 - \xi c_{2s})} \\ &\quad - \xi \frac{c_{1s} \kappa_{1s} \cos \alpha + c_{2s} \kappa_{2s} \sin \alpha + \nabla_s c_{2s} \cdot \mathbf{e}_{1s} \sin \alpha - \nabla_s c_{1s} \cdot \mathbf{e}_{2s} \cos \alpha}{(1 - \xi c_{1s})(1 - \xi c_{2s})} \\ &\quad - \xi \frac{c_{2s} \cos \alpha \nabla_s \alpha \cdot \mathbf{e}_{1s} + c_{1s} \sin \alpha \nabla_s \alpha \cdot \mathbf{e}_{2s}}{(1 - \xi c_{1s})(1 - \xi c_{2s})} \\ &= \frac{\nabla_s \alpha \cdot \mathbf{n}_s + \kappa_{1s} \cos \alpha + \kappa_{2s} \sin \alpha - \xi \operatorname{div}_s (c_{2s} \sin \alpha \mathbf{e}_{1s} - c_{1s} \cos \alpha \mathbf{e}_{2s})}{1 - 2H\xi + \kappa_{\mathbf{n}_s} x i^2} \\ &= \frac{\kappa_{\mathbf{n}_s} - \xi \boldsymbol{\nu}_s \cdot \operatorname{curl}_s (\mathbf{L} \mathbf{n}_s)}{1 - 2H\xi + \kappa_{\mathbf{n}_s} x i^2}\end{aligned}\quad (48)$$

and

$$\begin{aligned}\mathbf{t} \cdot (\nabla \mathbf{n}) \mathbf{t} &= \frac{-(\nabla_s \alpha \cdot \mathbf{e}_{1s}) \sin \alpha + (\nabla_s \alpha \cdot \mathbf{e}_{2s}) \cos \alpha - \kappa_{1s} \sin \alpha + \kappa_{2s} \cos \alpha}{(1 - \xi c_{1s})(1 - \xi c_{2s})} \\ &\quad - \xi \frac{-c_{1s} \kappa_{1s} \sin \alpha + c_{2s} \kappa_{2s} \cos \alpha + \nabla_s c_{2s} \cdot \mathbf{e}_{1s} \cos \alpha + \nabla_s c_{1s} \cdot \mathbf{e}_{2s} \sin \alpha}{(1 - \xi c_{1s})(1 - \xi c_{2s})} \\ &\quad + \xi \frac{c_{2s} \sin \alpha \nabla_s \alpha \cdot \mathbf{e}_{1s} - c_{1s} \cos \alpha \nabla_s \alpha \cdot \mathbf{e}_{2s}}{(1 - \xi c_{1s})(1 - \xi c_{2s})} \\ &= \frac{\nabla_s \alpha \cdot \mathbf{t}_s - \kappa_{1s} \sin \alpha + \kappa_{2s} \cos \alpha - \xi \operatorname{div}_s (c_{2s} \cos \alpha \mathbf{e}_{1s} + c_{1s} \sin \alpha \mathbf{e}_{2s})}{1 - 2H\xi + \kappa_{\mathbf{n}_s} x i^2} \\ &= \frac{\kappa_{\mathbf{t}_s} - \xi \boldsymbol{\nu}_s \cdot \operatorname{curl}_s (\mathbf{L} \mathbf{t}_s)}{1 - 2H\xi + \kappa_{\mathbf{n}_s} x i^2},\end{aligned}\quad (49)$$

where  $\mathbf{n}_s = \cos \alpha \mathbf{e}_{1s} + \sin \alpha \mathbf{e}_{2s}$  and  $\mathbf{t}_s = \boldsymbol{\nu}_s \times \mathbf{n}_s$  are the restrictions of  $\mathbf{n}$  and  $\mathbf{t}$  on  $\mathcal{S}$ , respectively, and  $\mathbf{L} = c_{1s} \mathbf{e}_{1s} \otimes \mathbf{e}_{1s} + c_{2s} \mathbf{e}_{2s} \otimes \mathbf{e}_{2s}$  is the extrinsic curvature tensor on  $\mathcal{S}$ . The quantities

$$c_{\mathbf{n}_s} = c_{1s} \cos^2 \alpha + c_{2s} \sin^2 \alpha \quad \text{and} \quad c_{\mathbf{t}_s} = c_{1s} \sin^2 \alpha + c_{2s} \cos^2 \alpha$$

are the normal curvatures of the flux lines of  $\mathbf{n}_s$  and  $\mathbf{t}_s$ , respectively, whereas

$$\tau_{\mathbf{n}_s} = (c_{1s} - c_{2s}) \sin \alpha \cos \alpha$$

is the geodesic torsion of the flux lines of  $\mathbf{n}_s$ . In deriving (48) and (49) we have made use of the Lioville's formula (see do Carmo (1976) page 253) for the calculation of the geodesic curvatures  $\kappa_{\mathbf{n}_s}$  and  $\kappa_{\mathbf{t}_s}$ , *i.e.*

$$\kappa_{\mathbf{n}_s} = \nabla_s \alpha \cdot \mathbf{n}_s + \kappa_{1s} \cos \alpha + \kappa_{2s} \sin \alpha, \quad \kappa_{\mathbf{t}_s} = \nabla_s \alpha \cdot \mathbf{t}_s - \kappa_{1s} \sin \alpha + \kappa_{2s} \cos \alpha,$$

and have employed the identity

$$\operatorname{div}_s (\boldsymbol{\nu}_s \times \mathbf{u}) = -\boldsymbol{\nu}_s \cdot \operatorname{curl}_s \mathbf{u} \quad (50)$$

that holds true for any smooth field  $\mathbf{u}$  defined on  $\mathcal{S}$ . We may then conclude that (43)–(49) yield (6).



## B Derivation of $W_{OZF}^S$ and $W_{el}^S$

In this section we shall derive the approximations of the energies (10) and (16) that are valid for a homogeneous nematic whenever  $\varepsilon \ll 1$ .

**Proposition 1** *Let  $\mathbf{n}$  and  $q$  be smooth fields defined on  $V$ . Assume  $\mathbf{n}$  to be a unit vector field such that*

$$\mathbf{n}(p) \cdot \boldsymbol{\nu}(p) = 0 \quad \forall p \in V$$

and

$$\mathbf{n}[p_S + \xi \boldsymbol{\nu}_s(p_S)] = \mathbf{n}(p_S) \quad \forall p_S \in \mathcal{S}, \forall \xi \in [-h/2, h/2], \quad (51)$$

and  $q$  a scalar-valued field such that

$$q[p_S + \xi \boldsymbol{\nu}_s(p_S)] = q(p_S) \in [-1, 1] \quad \forall p_S \in \mathcal{S}, \forall \xi \in [-h/2, h/2]. \quad (52)$$

Then, denoting by  $\text{vol}(V)$  the volume of  $V$ ,

$$\begin{aligned} \lim_{\varepsilon \rightarrow 0} \int_V \frac{\overline{M}_{ij,k} \overline{M}_{ij,k}}{\text{vol}(V)} dV &= \int_{\mathcal{S}} \frac{q^2 [(\text{div}_s \mathbf{n}_s)^2 + |\mathbf{n}_s \times \text{curl}_s \mathbf{n}_s|^2 + (\text{curl}_s \mathbf{n}_s \cdot \mathbf{n}_s)^2]}{\text{area}(\mathcal{S})} dA \\ &+ \int_{\mathcal{S}} \frac{\frac{|\nabla_s q|^2}{2} + 2(1-q)H[(1-q)H + 2qc_{\mathbf{n}_s}] - (1-q^2)K}{\text{area}(\mathcal{S})} dA, \end{aligned} \quad (53)$$

$$\begin{aligned} \lim_{\varepsilon \rightarrow 0} \int_V \frac{\overline{M}_{ij,j} \overline{M}_{ik,k}}{\text{vol}(V)} dV &= \int_{\mathcal{S}} \frac{q^2 [(\text{div}_s \mathbf{n}_s)^2 + |\mathbf{n}_s \times \text{curl}_s \mathbf{n}_s|^2]}{\text{area}(\mathcal{S})} dA \\ &+ \int_{\mathcal{S}} \frac{\frac{|\nabla_s q|^2}{4} - q \nabla_s q \cdot [(\text{curl}_s \mathbf{n}_s \cdot \boldsymbol{\nu}_s) \mathbf{t} - (\text{div}_s \mathbf{n}_s) \mathbf{n}_s] + (1-q)H[(1-q)H + 2qc_{\mathbf{n}_s}]}{\text{area}(\mathcal{S})} dA, \end{aligned} \quad (54)$$

$$\begin{aligned} \lim_{\varepsilon \rightarrow 0} \int_V \frac{(\overline{M}_{ij,k} \overline{M}_{jk} - \overline{M}_{ij} \overline{M}_{jk,k})_{,i}}{\text{vol}(V)} dV &= \int_{\mathcal{S}} \frac{2q \nabla_s q \cdot [(\text{curl}_s \mathbf{n}_s \cdot \boldsymbol{\nu}_s) \mathbf{t}_s - (\text{div}_s \mathbf{n}_s) \mathbf{n}_s]}{\text{area}(\mathcal{S})} dA \\ &- \int_{\mathcal{S}} \frac{(1-q^2)}{2\text{area}(\mathcal{S})} \kappa_{\mathbf{n}_s} dA, \end{aligned} \quad (55)$$

where

$$\overline{M}_{ij} = q n_i n_j + \frac{1}{2} (1-q) (\delta_{ij} - \nu_i \nu_j).$$

We observe that

$$\text{vol}(V) = h \left[ \text{area}(\mathcal{S}) + \frac{h^2}{12} \int_{\mathcal{S}} \kappa_{\mathbf{n}_s} dA \right]. \quad (56)$$

With the aid of equation (7)

$$\begin{aligned} \int_V \frac{q^2 (\text{div} \mathbf{n})^2}{\text{vol}(V)} dV &= \int_{-h/2}^{h/2} d\xi \int_{\mathcal{S}_\xi} \frac{q^2 [\kappa_{\mathbf{t}_s} - \xi \boldsymbol{\nu}_s \cdot \text{curl}_s(\mathbf{L} \mathbf{t}_s)]^2}{\iota^2 \text{vol}(V)} dA \\ &= \int_{-h/2}^{h/2} d\xi \int_{\mathcal{S}} \frac{q^2 [\kappa_{\mathbf{t}_s} - \xi \boldsymbol{\nu}_s \cdot \text{curl}_s(\mathbf{L} \mathbf{t}_s)]^2}{\iota \text{vol}(V)} dA \\ &= \int_{\mathcal{S}} \left\{ \int_{-h/2}^{h/2} \frac{q^2 [\kappa_{\mathbf{t}_s} - \xi \boldsymbol{\nu}_s \cdot \text{curl}_s(\mathbf{L} \mathbf{t}_s)]^2}{\iota \text{vol}(V)} dd\xi \right\} dA. \end{aligned}$$

Since  $q$ ,  $\kappa_{\mathbf{t}_s}$  and  $\boldsymbol{\nu}_s \cdot \text{curl}_s(\mathbf{L}\mathbf{t}_s)$  do not depend on  $\xi$ , by means of (56) we deduce that

$$\int_{-h/2}^{h/2} \frac{q^2[\kappa_{\mathbf{t}_s} - \xi \boldsymbol{\nu}_s \cdot \text{curl}_s(\mathbf{L}\mathbf{t}_s)]^2}{\iota h \left( \text{area}(\mathcal{S}) + \frac{h^2}{12} \int_{\mathcal{S}} \kappa_{\mathbf{n}_s} dA \right)} d\xi \rightarrow \frac{q^2 \kappa_{\mathbf{t}_s}^2}{\text{area}(\mathcal{S})}$$

uniformly in  $\mathcal{S}$  as  $\varepsilon \rightarrow 0$ . Therefore, recalling (9)<sub>1</sub>,

$$\lim_{\varepsilon \rightarrow 0} \int_V \frac{q^2(\text{div} \mathbf{n})^2}{\text{vol}(V)} dV = \int_{\mathcal{S}} \frac{q^2(\text{div}_s \mathbf{n}_s)^2}{\text{area}(\mathcal{S})} dA. \quad (57)$$

We now use equation (8) to obtain

$$\int_V \frac{q^2(\text{curl} \mathbf{n} \cdot \mathbf{n})^2}{\text{vol}(V)} dV = \int_{\mathcal{S}} \left[ \int_{-h/2}^{h/2} \frac{q^2 \tau^2}{\iota \text{vol}(V)} d\xi \right] dA$$

and

$$\int_V \frac{q^2 |\mathbf{n} \times \text{curl} \mathbf{n}|^2}{\text{vol}(V)} dV = \int_{\mathcal{S}} \left\{ \int_{-h/2}^{h/2} \frac{q^2 (c_{\mathbf{n}_s} - \kappa_{\mathbf{n}_s} xi)^2 + [\kappa_{\mathbf{n}_s} - \xi \boldsymbol{\nu}_s \cdot \text{curl}_s(\mathbf{L}\mathbf{n}_s)]^2}{\iota \text{vol}(V)} d\xi \right\} dA.$$

Considering that  $q$ ,  $c_{\mathbf{n}_s}$ ,  $\tau_{\mathbf{n}_s}$ ,  $\kappa_{\mathbf{n}_s}$  and  $\boldsymbol{\nu}_s \cdot \text{curl}_s(\mathbf{L}\mathbf{n}_s)$  do not depend on  $\xi$ , by means of (56), we have

$$\int_{-h/2}^{h/2} \frac{q^2 \tau_{\mathbf{n}_s}^2}{\iota h \left( \text{area}(\mathcal{S}) + \frac{h^2}{12} \int_{\mathcal{S}} \kappa_{\mathbf{n}_s} dA \right)} d\xi \rightarrow \frac{q^2 \tau_{\mathbf{n}_s}^2}{\text{area}(\mathcal{S})} \quad \text{uniformly in } \mathcal{S} \text{ as } \varepsilon \rightarrow 0$$

and

$$\int_{-h/2}^{h/2} q^2 \frac{(c_{\mathbf{n}_s} - \kappa_{\mathbf{n}_s} xi)^2 + [\kappa_{\mathbf{n}_s} - \xi \boldsymbol{\nu}_s \cdot \text{curl}_s(\mathbf{L}\mathbf{n}_s)]^2}{\iota h \left( \text{area}(\mathcal{S}) + \frac{h^2}{12} \int_{\mathcal{S}} \kappa_{\mathbf{n}_s} dA \right)} d\xi \rightarrow \frac{q^2 (c_{\mathbf{n}_s}^2 + \kappa_{\mathbf{n}_s}^2)}{\text{area}(\mathcal{S})}$$

uniformly in  $\mathcal{S}$  as  $\varepsilon \rightarrow 0$ . Thus, from (9) we deduce that

$$\lim_{\varepsilon \rightarrow 0} \int_V \frac{q^2 (\mathbf{n} \cdot \text{curl} \mathbf{n})^2}{\text{vol}(V)} dV = \int_{\mathcal{S}} \frac{q^2 (\mathbf{n}_s \cdot \text{curl}_s \mathbf{n}_s)^2}{\text{area}(\mathcal{S})} dA \quad (58)$$

and

$$\lim_{\varepsilon \rightarrow 0} \int_V \frac{q^2 |\mathbf{n} \times \text{curl} \mathbf{n}|^2}{\text{vol}(V)} dV = \int_{\mathcal{S}} \frac{q^2 |\mathbf{n}_s \times \text{curl}_s \mathbf{n}_s|^2}{\text{area}(\mathcal{S})} dA. \quad (59)$$

By following the same arguments which lead to (57)–(59) and by taking into account that

$$\nabla q = \frac{\nabla_s q \cdot \mathbf{e}_{1s}}{1 - \xi c_{1s}} \mathbf{e}_1 + \frac{\nabla_s q \cdot \mathbf{e}_{2s}}{1 - \xi c_{2s}} \mathbf{e}_2,$$

one can easily prove that

$$\lim_{\varepsilon \rightarrow 0} \int_V \frac{|\nabla q|^2}{\text{vol}(V)} dV = \int_{\mathcal{S}} \frac{|\nabla_s q|^2}{\text{area}(\mathcal{S})} dA, \quad (60)$$

$$\begin{aligned} \lim_{\varepsilon \rightarrow 0} \int_V \frac{(1-q)(H - \kappa_{\mathbf{n}_s} \xi)}{\iota^2 \text{vol}(V)} [(1-q)H + 2q c_{\mathbf{n}_s} - (1+q) \kappa_{\mathbf{n}_s} xi] \\ = \int_{\mathcal{S}} \frac{(1-q)H}{\text{area}(\mathcal{S})} [(1-q)H + 2q c_{\mathbf{n}_s}] dA, \end{aligned} \quad (61)$$

$$\lim_{\varepsilon \rightarrow 0} \int_V \frac{(1-q^2)K}{\iota^2 \text{vol}(V)} dV = \int_S \frac{(1-q^2)K}{\text{area}(\mathcal{S})} dA, \quad (62)$$

$$\begin{aligned} \lim_{\varepsilon \rightarrow 0} \int_V \frac{q \nabla q \cdot [(\nabla \mathbf{n})\mathbf{n} - (\text{div} \mathbf{n})\mathbf{n}]}{\text{vol}(V)} dV \\ = \int_S \frac{q \nabla_s q \cdot [(\text{curl}_s \mathbf{n}_s \cdot \boldsymbol{\nu}_s) \mathbf{t}_s - (\text{div}_s \mathbf{n}_s) \mathbf{n}_s]}{\text{area}(\mathcal{S})} dA. \end{aligned} \quad (63)$$

Now, let us assume now that  $\mathcal{S}$  is a regular surface whose boundary  $\partial \mathcal{S}$  is a regular curve, and let  $\boldsymbol{\tau}$  be the tangent unit vector field to  $\partial \mathcal{S}$ . Then, the normal unit vector field to the surface

$$\mathcal{S}_\iota := \{p_{\partial \mathcal{S}} + \xi \boldsymbol{\nu}_s(p_{\partial \mathcal{S}}) : p_{\partial \mathcal{S}} \in \partial \mathcal{S}, \xi \in [-h/2, h/2]\}$$

is

$$\mathbf{N} = \frac{(\boldsymbol{\tau} - \xi \mathbf{L} \boldsymbol{\tau}) \times \boldsymbol{\nu}}{|(\boldsymbol{\tau} - \xi \mathbf{L} \boldsymbol{\tau}) \times \boldsymbol{\nu}|}.$$

Therefore, by means of the divergence theorem we deduce that

$$\begin{aligned} \int_V \text{div} \left\{ \iota^{-1} (1-q) [(1-q)H + 2qc_{\mathbf{n}_s} - (1+q)\kappa_{\mathbf{n}_s} \, xi] \boldsymbol{\nu} \right\} dV \\ = \int_{\mathcal{S}_{h/2}} \frac{1-q}{1-Hh + \kappa_{\mathbf{n}_s} h^2/4} \left[ (1-q)H + 2qc_{\mathbf{n}_s} - (1+q)\kappa_{\mathbf{n}_s} \frac{h}{2} \right] dA \\ - \int_{\mathcal{S}_{-h/2}} \frac{1-q}{1+Hh + \kappa_{\mathbf{n}_s} h^2/4} \left[ (1-q)H + 2qc_{\mathbf{n}_s} + (1+q)\kappa_{\mathbf{n}_s} \frac{h}{2} \right] dA \\ + \int_{\mathcal{S}_\iota} \iota^{-1} (1-q) [(1-q)H + 2qc_{\mathbf{n}_s} - (1+q)\kappa_{\mathbf{n}_s} \, xi] \boldsymbol{\nu} \cdot \mathbf{N} dA \\ = \int_S (1-q) \left[ (1-q)H + 2qc_{\mathbf{n}_s} - (1+q)\kappa_{\mathbf{n}_s} \frac{h}{2} \right] dA \\ - \int_S (1-q) \left[ (1-q)H + 2qc_{\mathbf{n}_s} + (1+q)\kappa_{\mathbf{n}_s} \frac{h}{2} \right] dA = - \int_S h(1-q^2) \kappa_{\mathbf{n}_s} dA. \end{aligned}$$

By means of (56) we may conclude that

$$\begin{aligned} \lim_{\varepsilon \rightarrow 0} \int_V \text{div} \left\{ \frac{(1-q)}{\iota \text{vol}(V)} [(1-q)H + 2qc_{\mathbf{n}_s} - (1+q)\kappa_{\mathbf{n}_s} \, xi] \boldsymbol{\nu} \right\} dV \\ = - \lim_{\varepsilon \rightarrow 0} \int_S \frac{(1-q^2)K}{\text{area}(\mathcal{S}) + \frac{h^2}{12} \int_S \kappa_{\mathbf{n}_s} dA} dA = - \int_S \frac{(1-q^2)K}{\text{area}(\mathcal{S})} dA. \end{aligned} \quad (64)$$

We arrive at (64) also whenever  $\mathcal{S}$  is a geometrically closed surface, i.e.,  $\partial \mathcal{S} = \emptyset$ .

Finally, equations (53)–(55) immediately follows from (19)–(22) and (57)–(64).

From (56) it follows that

$$\lim_{\varepsilon \rightarrow 0} \text{vol}(V) = h \text{area}(\mathcal{S}). \quad (65)$$

As an immediate consequence of Proposition 1 and (65), we have

$$\begin{aligned} W_{el}(\nabla \mathbf{Q}, \mathbf{Q}) = \text{vol}(V) \left\{ \int_V \frac{L_1 \overline{M}_{ij,k} \overline{M}_{ij,k} + L_2 \overline{M}_{ij,j} \overline{M}_{ik,k}}{\text{vol}(V)} dV \right. \\ \left. + \int_V \frac{L_{24} (\overline{M}_{ij,k} \overline{M}_{jk} - \overline{M}_{ij} \overline{M}_{jk,k})_{,i}}{\text{vol}(V)} dV \right\} \approx W_{el}^S \quad \text{for } \varepsilon \ll 1, \end{aligned}$$

with  $W_{el}^S$  as in (23).

On taking  $q \equiv 1$  in (57)–(59) we have the following

**Proposition 2** *Let  $\mathbf{n}$  be a smooth unit vector field defined on  $V$  such that*

$$\mathbf{n}(p) \cdot \boldsymbol{\nu}(p) = 0 \quad \forall p \in V$$

*and*

$$\mathbf{n}(p_S + \xi \boldsymbol{\nu}_s) = \mathbf{n}(p_S) \quad \forall p_S \in \mathcal{S}, \forall \xi \in [-h/2, h/2].$$

*Then*

$$\lim_{\varepsilon \rightarrow 0} \int_V \frac{(\operatorname{div} \mathbf{n})^2}{\operatorname{vol}(V)} dV = \int_{\mathcal{S}} \frac{(\operatorname{div}_s \mathbf{n}_s)^2}{\operatorname{area}(\mathcal{S})} dA, \quad (66)$$

$$\lim_{\varepsilon \rightarrow 0} \int_V \frac{(\mathbf{n} \cdot \operatorname{curl} \mathbf{n})^2}{\operatorname{vol}(V)} dV = \int_{\mathcal{S}} \frac{(\mathbf{n}_s \cdot \operatorname{curl}_s \mathbf{n}_s)^2}{\operatorname{area}(\mathcal{S})} dA, \quad (67)$$

$$\lim_{\varepsilon \rightarrow 0} \int_V \frac{|\mathbf{n} \times \operatorname{curl} \mathbf{n}|^2}{\operatorname{vol}(V)} dV = \int_{\mathcal{S}} \frac{|\mathbf{n}_s \times \operatorname{curl}_s \mathbf{n}_s|^2}{\operatorname{area}(\mathcal{S})} dA. \quad (68)$$

Therefore, from (13), Proposition 2 and (65), it follows that

$$W_{OZF} = \operatorname{vol}(V) \int_V \frac{K_1(\operatorname{div} \mathbf{n})^2 + K_2(\mathbf{n} \cdot \operatorname{curl} \mathbf{n})^2 + K_3|\mathbf{n} \times \operatorname{curl} \mathbf{n}|^2}{\operatorname{vol}(V)} dV \approx W_{OZF}^S$$

for  $\varepsilon \ll 1$ , with  $W_{OZF}^S$  as in (14).

## C Geometrical identities

Let us consider the orthogonal parameterization of  $\mathcal{S}$  introduced in Appendix A and set

$$x_1 = u, \quad x_2 = v, \quad \mathbf{g}_1 = \boldsymbol{\varphi}_{,u} = \sqrt{E} \mathbf{e}_{1s}, \quad \mathbf{g}_2 = \boldsymbol{\varphi}_{,v} = \sqrt{G} \mathbf{e}_{2s}.$$

The metric tensor induced on  $\mathcal{S}$  by the Euclidean metric tensor, written with respect to the system of local coordinates  $(x_1, x_2)$ , is

$$g = E dx^1 \otimes dx^1 + G dx^2 \otimes dx^2.$$

The Levi-Civita connection associated with the metric  $g$  is defined by the Christoffel symbols

$$\begin{aligned} \Gamma_{11}^1 &= \frac{E_{,u}}{2E}, \quad \Gamma_{11}^2 = -\frac{E_{,v}}{2G} = \frac{E}{\sqrt{G}} \kappa_{1s}, \quad \Gamma_{12}^1 = \Gamma_{21}^1 = \frac{E_{,v}}{2E} = -\sqrt{G} \kappa_{1s}, \\ \Gamma_{12}^2 &= \Gamma_{21}^2 = \frac{G_{,u}}{2G} = \sqrt{E} \kappa_{2s}, \quad \Gamma_{22}^1 = -\frac{G_{,u}}{2E} = -\frac{G}{\sqrt{E}} \kappa_{2s}, \quad \Gamma_{22}^2 = \frac{G_{,v}}{2G}. \end{aligned} \quad (69)$$

Then, the  $(0, 4)$  curvature tensor of  $\mathcal{S}$  has components

$$\begin{aligned} R_{\beta\gamma\delta\rho} &= g_{\rho\mu} \left( \frac{\partial \Gamma_{\gamma\delta}^\mu}{\partial x_\beta} - \frac{\partial \Gamma_{\beta\delta}^\mu}{\partial x_\gamma} + \Gamma_{\gamma\delta}^\lambda \Gamma_{\beta\lambda}^\mu - \Gamma_{\beta\delta}^\lambda \Gamma_{\gamma\lambda}^\mu \right) \\ &= EG (\nabla_s \kappa_{2s} \cdot \mathbf{e}_{1s} - \nabla_s \kappa_{1s} \cdot \mathbf{e}_{2s} + \kappa_{1s}^2 + \kappa_{2s}^2) \epsilon_{\beta\gamma} \epsilon_{\delta\rho} \\ &= -EG (\boldsymbol{\nu}_s \cdot \operatorname{curl}_s \boldsymbol{\omega}) \epsilon_{\beta\gamma} \epsilon_{\delta\rho} \quad (\beta, \gamma, \delta, \rho, \mu, \lambda = 1, 2), \end{aligned} \quad (70)$$

where  $\epsilon_{\beta\gamma} = \delta_{1\beta}\delta_{2\gamma} - \delta_{1\gamma}\delta_{2\beta}$  is the antisymmetric symbol and  $\boldsymbol{\omega} = -(\kappa_{1s}\mathbf{e}_{1s} + \kappa_{2s}\mathbf{e}_{2s})$  is the vector that parameterizes the spin connection  $\Omega_{\beta\gamma\delta}$  (see Bowick and Giomi (2009)), that is

$$\Omega_{\beta\gamma\delta} = \mathbf{e}_\gamma \cdot (D\mathbf{e}_\delta)\mathbf{e}_\beta = \omega_\beta \epsilon_{\gamma\delta} \quad (\beta, \gamma, \delta = 1, 2),$$

where  $D = \mathbf{P}\nabla_s$  is the usual covariant derivative (see Gurtin and Murdoch (1975)). It is well known that the Gaussian curvature of a surface equals the scalar curvature (see do Carmo (1992)). Therefore

$$\kappa_{\mathbf{n}_s} = \frac{1}{2} \sum_{\beta \neq \gamma} \frac{R_{\beta\gamma\beta\gamma}}{\det g} = -\boldsymbol{\nu}_s \cdot \text{curl}_s \boldsymbol{\omega}. \quad (71)$$

By means of (71) we can prove identity (25). We first observe that  $\kappa_{\mathbf{n}_s}\mathbf{n}_s + \kappa_{\mathbf{t}_s}\mathbf{t}_s = \nabla_s \alpha - \boldsymbol{\omega}$ , by which  $\kappa_{\mathbf{n}_s}\mathbf{t}_s - \kappa_{\mathbf{t}_s}\mathbf{n}_s = \boldsymbol{\nu}_s \times (\nabla_s \alpha - \boldsymbol{\omega})$ , with  $\alpha$  as in Section 3. Next, we recall the identity

$$\boldsymbol{\nu}_s \cdot \text{curl}_s(\nabla_s f) = 0, \quad (72)$$

that is valid for any smooth scalar field  $f$  defined on  $\mathcal{S}$ . Then, applying the surface divergence theorem and identities (50), (71) and (72) lead to

$$\begin{aligned} \int_{\mathcal{S}} q(\nabla_s q) \cdot (\kappa_{\mathbf{n}_s}\mathbf{t} - \kappa_{\mathbf{t}_s}\mathbf{n}) dA &= \frac{1}{2} \int_{\mathcal{S}} \text{div}_s [q^2 \boldsymbol{\nu}_s \times (\nabla_s \alpha - \boldsymbol{\omega})] dA \\ &\quad - \frac{1}{2} \int_{\mathcal{S}} q^2 \text{div}_s [\boldsymbol{\nu}_s \times (\nabla_s \alpha - \boldsymbol{\omega})] dA \\ &= \frac{1}{2} \int_{\partial\mathcal{S}} q^2 [\boldsymbol{\nu}_s \times (\nabla_s \alpha - \boldsymbol{\omega})] \cdot \mathbf{k} dl + \frac{1}{2} \int_{\mathcal{S}} q^2 \boldsymbol{\nu}_s \cdot \text{curl}_s(\nabla_s \alpha - \boldsymbol{\omega}) dA \\ &= \frac{1}{2} \int_{\partial\mathcal{S}} q^2 (\nabla_s \alpha - \boldsymbol{\omega}) \cdot d\mathbf{l} + \frac{1}{2} \int_{\mathcal{S}} q^2 K dA, \end{aligned}$$

where  $\mathbf{k}$  is the outward normal to the boundary  $\partial\mathcal{S}$  lying on the tangent plane.

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